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Title: Compositional and defect evolution under irradiation

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# Compositional and defect evolution under irradiation

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**LANL**

# Compositional and defect evolution under irradiation

**Continuum description:**

Wiedersich formalism:

Valid in 1 phase regions

$$J_A = -\left(d^c_{AV}C_V + d^c_{AI}C_I\right)\Phi\nabla C_A + C_A\left(d_{AV}\nabla C_V - d_{AI}\nabla C_I\right)$$
$$J_B = -\left(d^c_{BV}C_V + d^c_{BI}C_I\right)\Phi\nabla C_B + C_B\left(d_{BV}\nabla C_V - d_{BI}\nabla C_I\right)$$
$$J_V = -\left(C_A d_{AV} + C_B d_{BV}\right)\nabla C_V + C_V\Phi\left(d^c_{AV}\nabla C_A + d^c_{BV}\nabla C_B\right)$$
$$J_I = -\left(C_A d_{AI} + C_B d_{BI}\right)\nabla C_I - C_I\Phi\left(d^c_{AI}\nabla C_A + d^c_{BI}\nabla C_B\right)$$

Irreversible thermodynamics:

Valid in multi-phase regions

$$\mathbb{J} = \mathcal{L}\mathbb{X} = \mathcal{L}\nabla\mu$$

**Atomistic approaches:** Computationally more demanding but also more accurate

Molecular Dynamics: Solves the entire process with no rare event assumptions, for a given interatomic potential

- Time limitation → might be valid for fast species like SIA
- No limitation in terms of lattice mismatch or phase transformations

Kinetic Monte Carlo: For rare event processes

- Longer time scales
- Assumptions might be included in the definition of events and calculation of rates.

# Calculation of the bulk free energy

## Thermodynamic Integration:

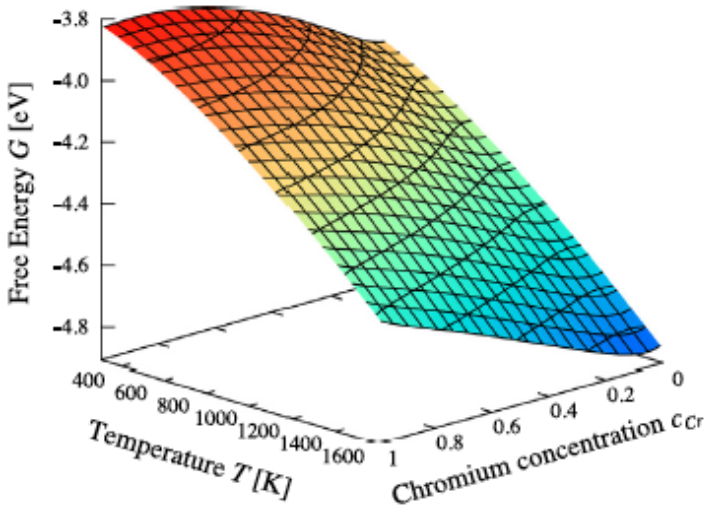
$$H_a(x) = x(1-x)\left[\sum_{i=0}^{5} a_i(1-2x)^i\right] + a_6 x + a_7(1-x)$$

$$H_{\xi\in\{b,c,d\}}(c) = \sum_{i=0}^{3} \xi_i \cdot (1-x)^i$$

$$H_e(x) = -\frac{H_a(x)}{T_0} + H_c(x)T_0 + H_b(x)\log T_0 + H_d(x)\frac{T_0^2}{2}$$

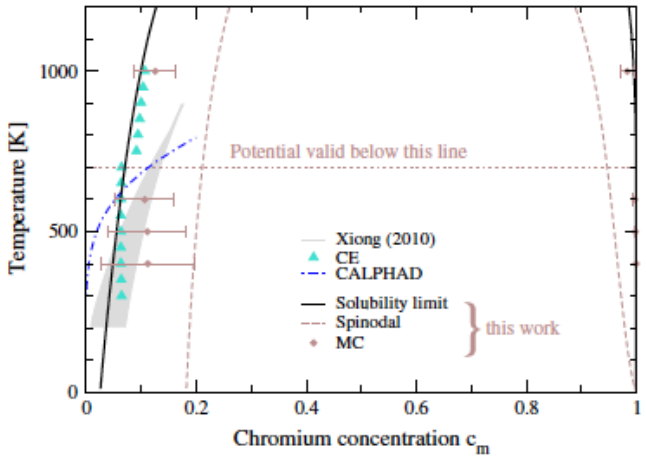
$$G_0(x) = x(1-x)\left[\sum_{i=0}^{5} f_i(1-2x)^i\right] + f_6 x + f_7(1-x)$$

$$G(x,T) = G_0(x)\frac{T}{T_0} + H_a(x) - H_b(x)T\log T - H_c(x)T^2 + H_d(x)\frac{T^3}{2} + H_e(x)T + Tk_B(x\log x + (1-x)\log(1-x))$$




## Monte Carlo VC-SGC:

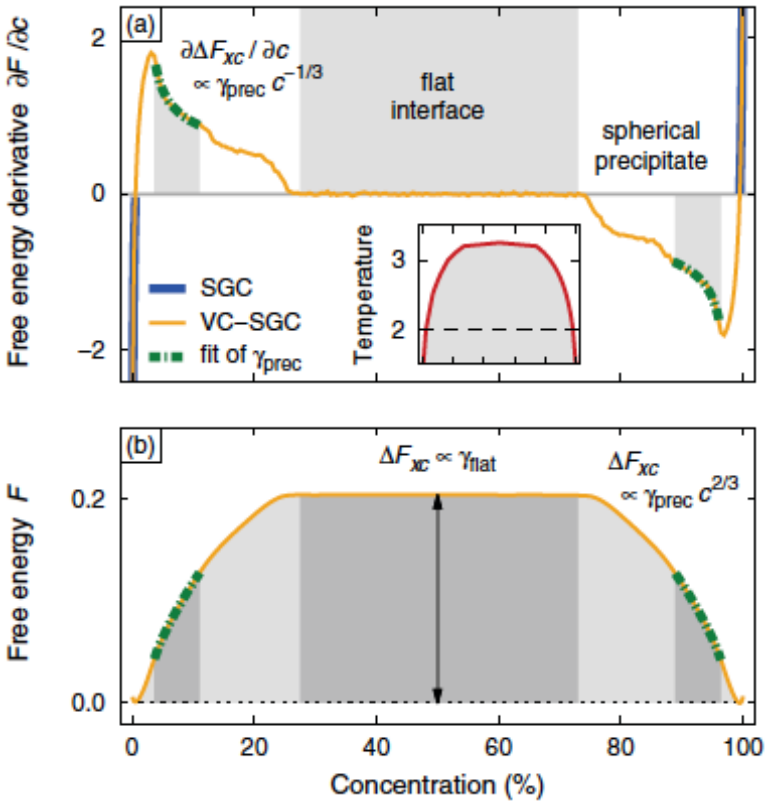
$$\pi_V(x^{3N},\sigma^N;\phi,\kappa,\mathcal{N}) \propto \exp[-\beta U(x^{3N},\sigma^N)] \times \exp\left\{-\beta\kappa\left[N\hat{c}(\sigma^N) + \frac{\phi}{2\kappa}\right]^2\right\}.$$

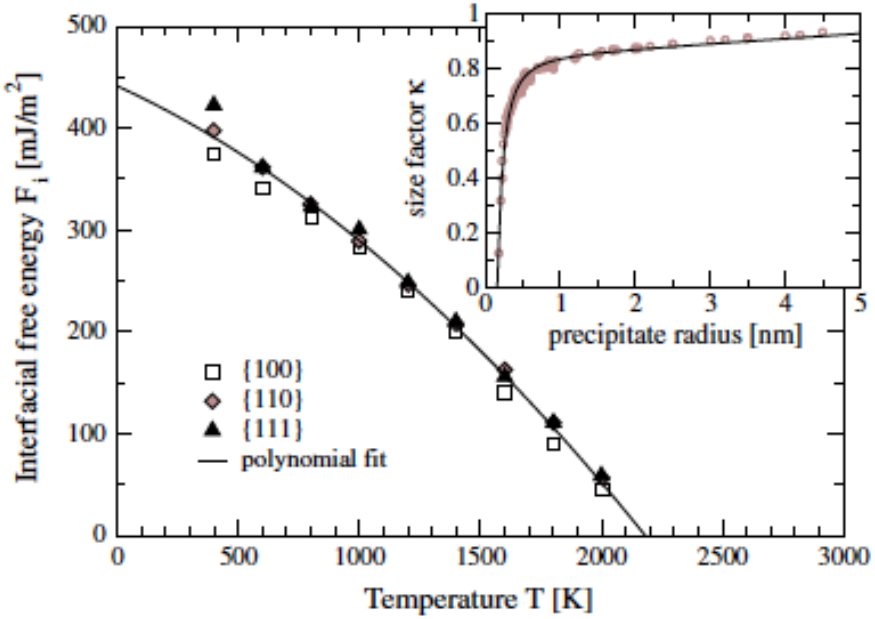



**Automated calculation of free energies within LAMMPS (including vibrational entropies)**

# Calculation of the interfacial free energy

## Monte Carlo VC-SGC:




**With VC-SGC we have access to all the concentration range**

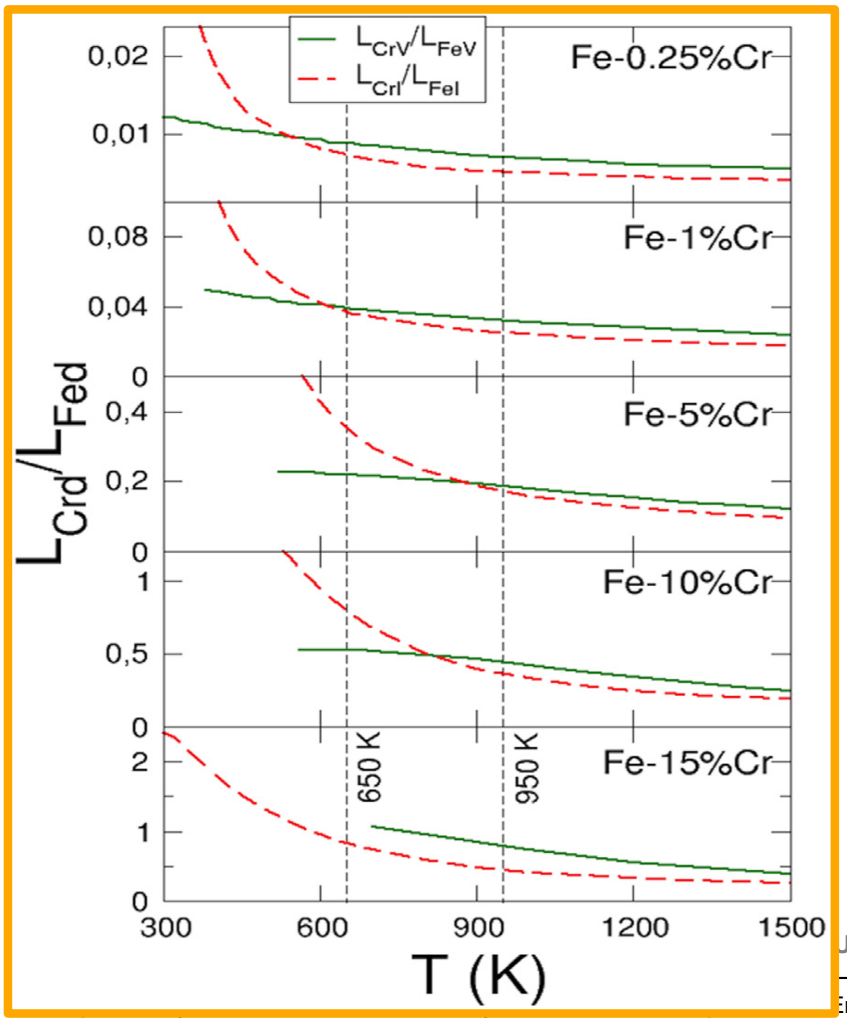
# Transport coefficients

## Kinetic Monte Carlo:

**The coupling is controlled by the cross-coefficients of the Onsager matrix**

$$J_B = -\sum_{\alpha} L_{B\alpha} \nabla \mu_\alpha$$

$$\text{AKMC:} \quad L_{ij} \propto \frac{\langle R_i . R_j \rangle}{6t}$$




Wiedersich at steady-state:

$$\nabla X_{Cr} = \frac{L_{FeI} L_{FeV}}{X_V \left( L_{FeI} D_{Cr} + L_{CrI} D_{Fe} \right)} \left( \frac{L_{CrV}}{L_{FeV}} - \frac{L_{CrI}}{L_{FeI}} \right) \nabla X_V$$

Assuming no precipitation occurs and $L_{\alpha\beta}$ are independent of local composition enrichment or depletion is controlled by the sign of

$$\left( \frac{L_{CrV}}{L_{FeV}} - \frac{L_{CrI}}{L_{FeI}} \right)$$

These Onsager coefficients for the whole concentration range are inputs to Phase Field models

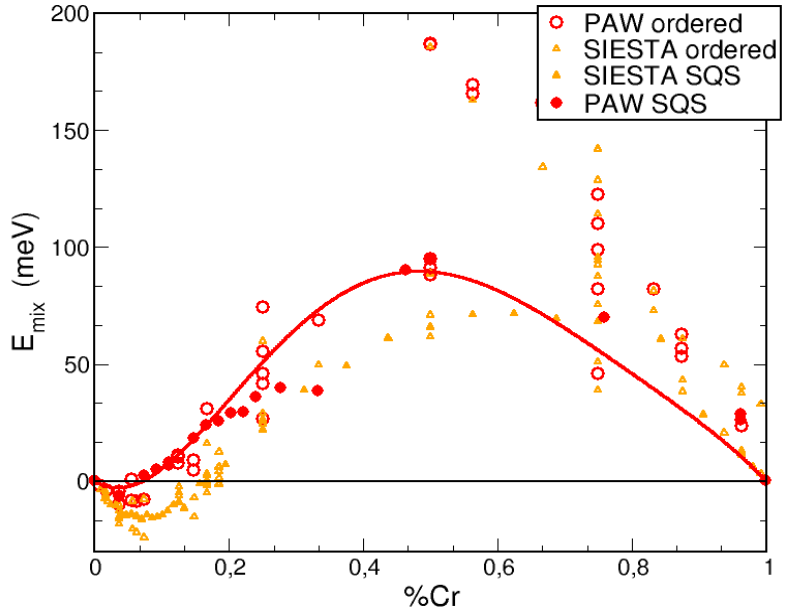
In principle we could use MD to calculate the same quantities. MD will run into the time scale problem, but we could rely on AMD methods in that case.

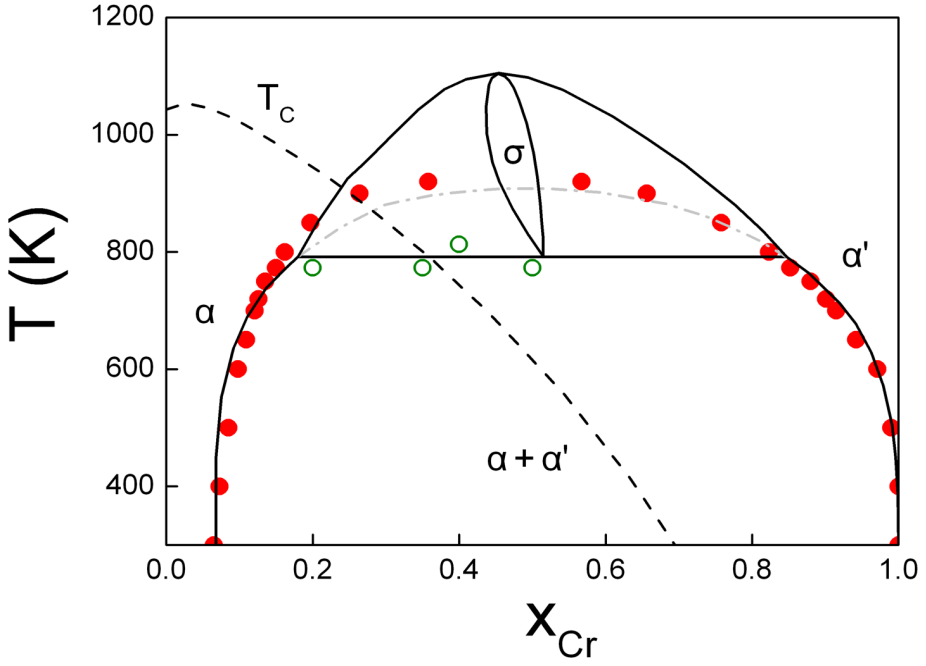
# Thermodynamics : DFT calculations and interaction model

**Pair interactions on a rigid BCC lattice:** free energy of one atomic configuration $G_{conf} = \sum_{ij} g_{ij}^{(n)}$

FeCr alloys :

- temperature dependent interactions → entropies of vibration
- composition dependent interactions → effects of the magnetic transitions.




**Phase diagram** : good agreement with the modified CALPHAD diagram (Bonny et al, 2010)
→ asymmetrical miscibility gap, non-vanishing Cr solubility at low T

# Kinetics: Rigid lattice diffusion model

- **Simulation of a A-B alloy in a rigid lattice**
- **Diffusion by thermally activated vacancy jumps**
  - jump frequency : depend on the local environments

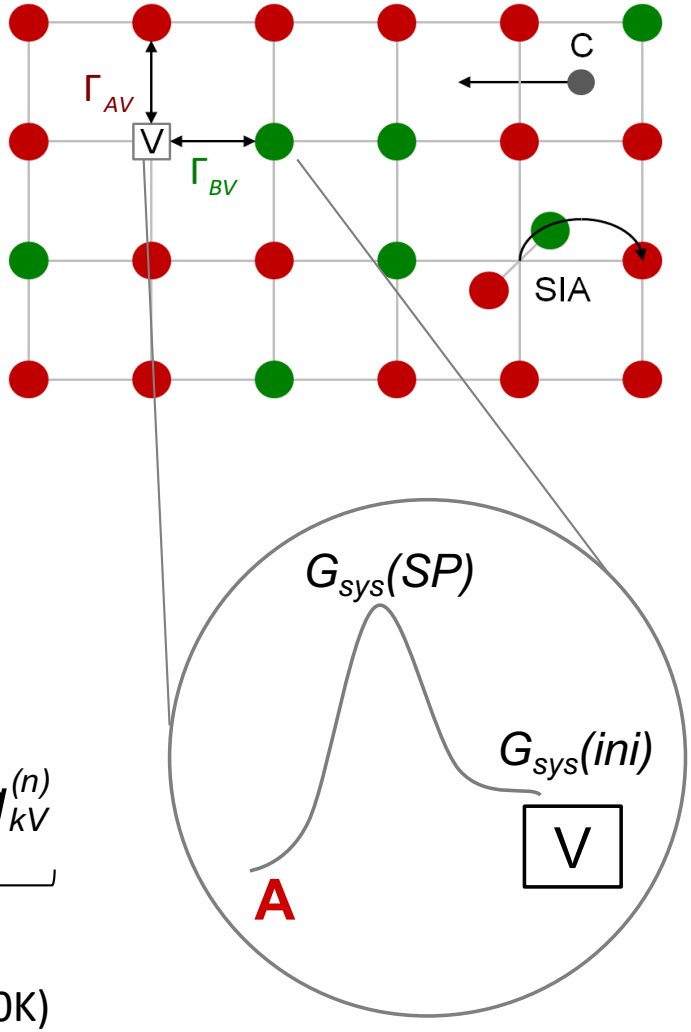
$$\Gamma_{AV} = \nu_A \exp\left(-\frac{\Delta G^{mig}_{AV}}{k_B T}\right)$$

  - migration barriers: broken-bond models

$$G_{syst} = \underbrace{H - TS_{nc}}_{\sum_i g_{ij}} - TS_{conf}$$

$$\Delta G^{mig}_{AV} = G_{sys}(SP) - G_{sys}(ini) = \underbrace{\sum_i g^{SP}_{Ai}}_{\text{saddle-point interactions}} - \underbrace{\sum_{j,n} g^{(n)}_{Aj} - \sum_{k,n} g^{(n)}_{kV}}_{\text{broken-bonds}}$$

fitted on DFT calculations (0K)



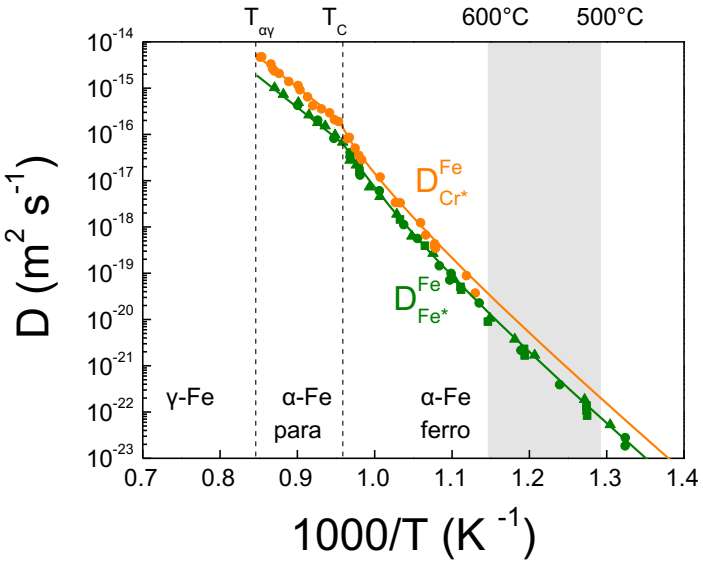

**Stress effects could be added using a dipolar tensor approximation**

# Kinetics: Rigid Lattice Diffusion Model

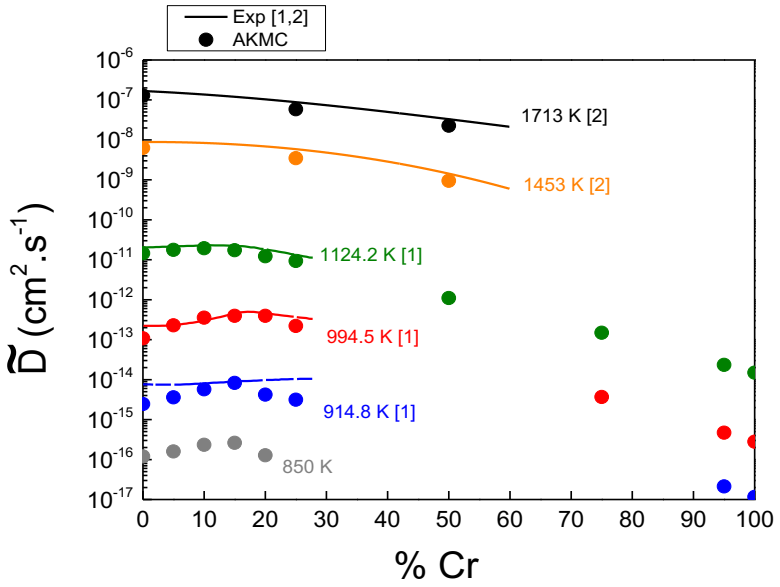
- At 0K : DFT calculations of vacancy/interstitial migration barriers → saddle-point interactions

- Acceleration at the ferro-paramagnetic transition in the α phase → corrections of the migration barriers, fit on experimental tracer and interdiffusion coefficients

Tracer diffusion coefficients in iron




Interdiffusion coefficient

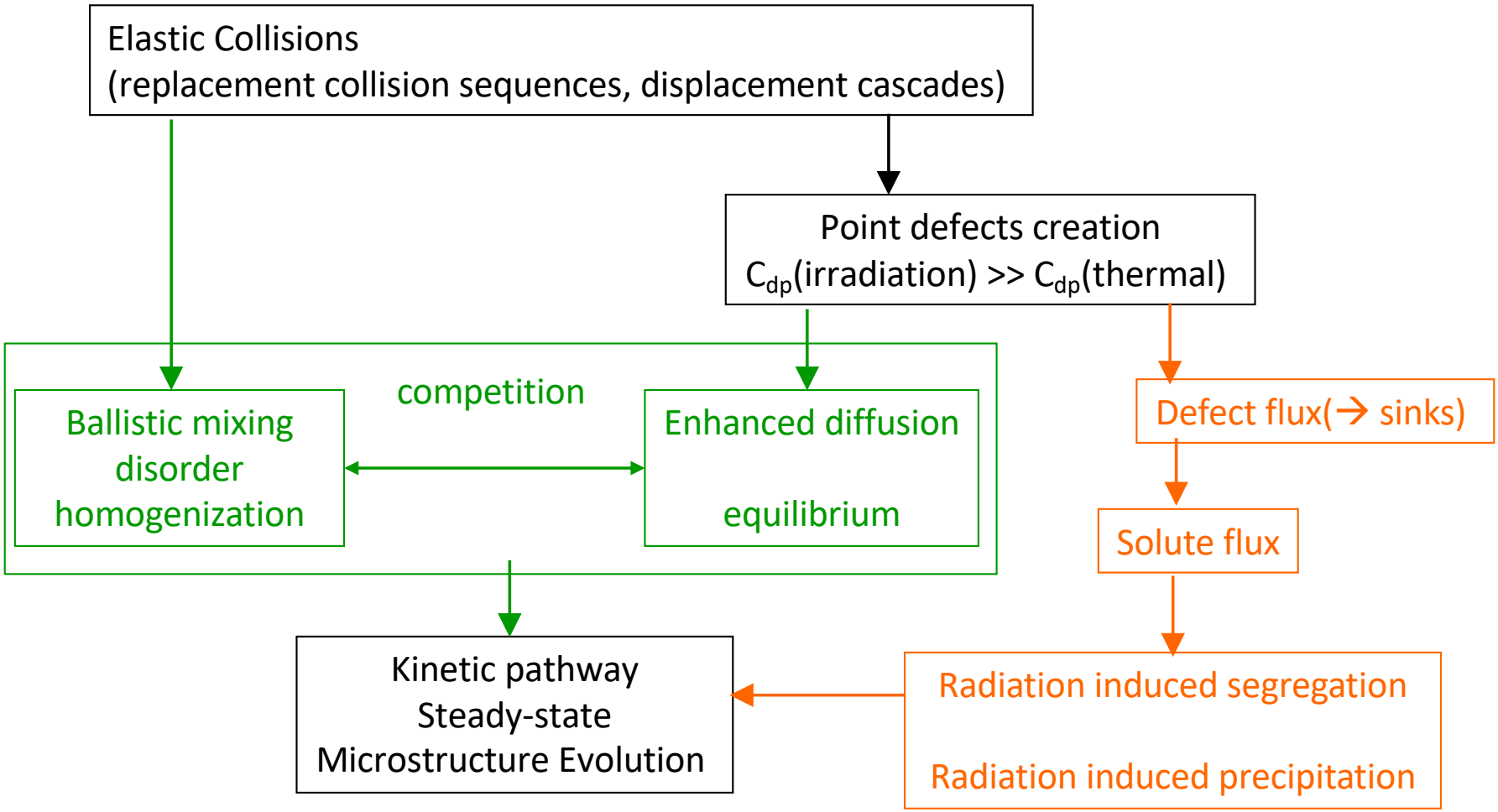



**The experimental diffusion coefficients are well reproduced**




[1] Braun & Feller-Kniepmeier, 1985
[2] Jönsson 1995

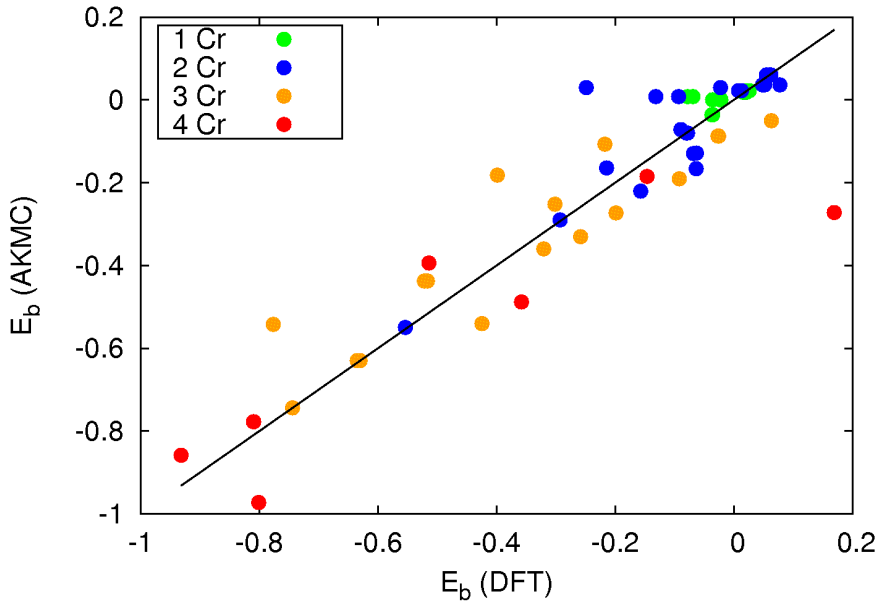
# Under Irradiation: Long-term Behavior

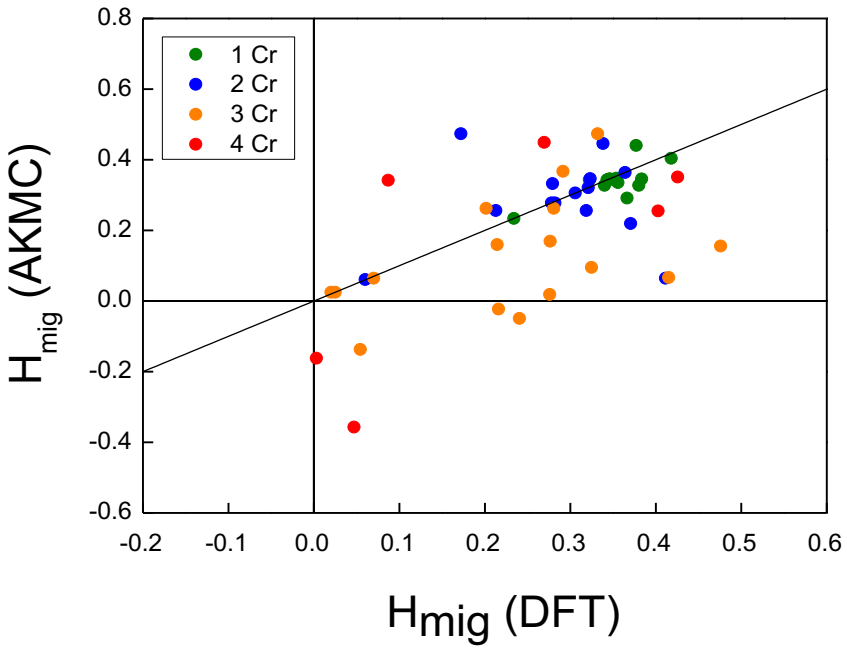


# Under Irradiation: Self-Interstitial Diffusion

**DFT calculations of SIA properties in Fe, Cr and dilute FeCr alloys (PWSCF, GGA-PAW)**
similar to Olsson et al. PRB 2007, JNM 2009

**Integration of <110> dumbbell diffusion in the AKMC code**




**- the binding energies are well reproduced**
**- the description of the migration barriers need improvement for concentrated alloys**

# Radiation-Induced Segregation: Interface Spacing Effect

**KMC shows a linear dependence of the amount of segregation with the interface spacing**

$$S^{Cr} = \sum_{i}^{N_p/2} l_z \left(X_i - X_0\right) \approx \int_0^{h/2} \left(X_{Cr}(z) - X_{Cr}(0)\right) dz = \frac{h}{2} X_{Cr}^{nominal} - \frac{h}{2} X_{Cr}(0)$$

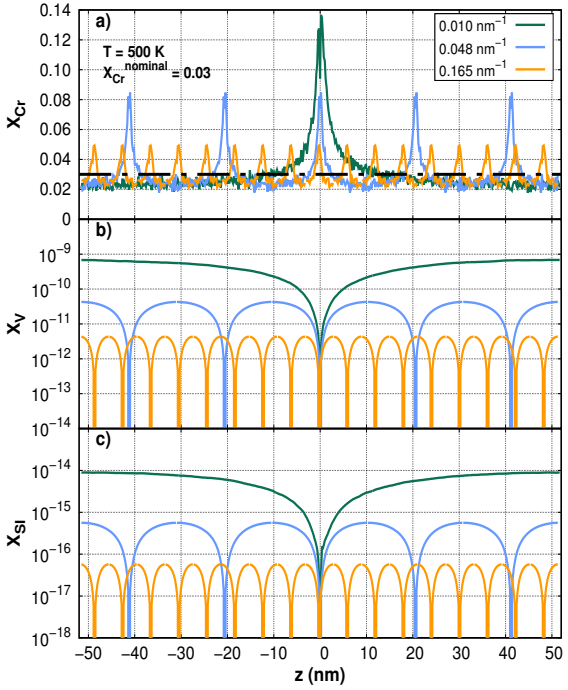
In the kinetic regime, and analytical expression can be found.

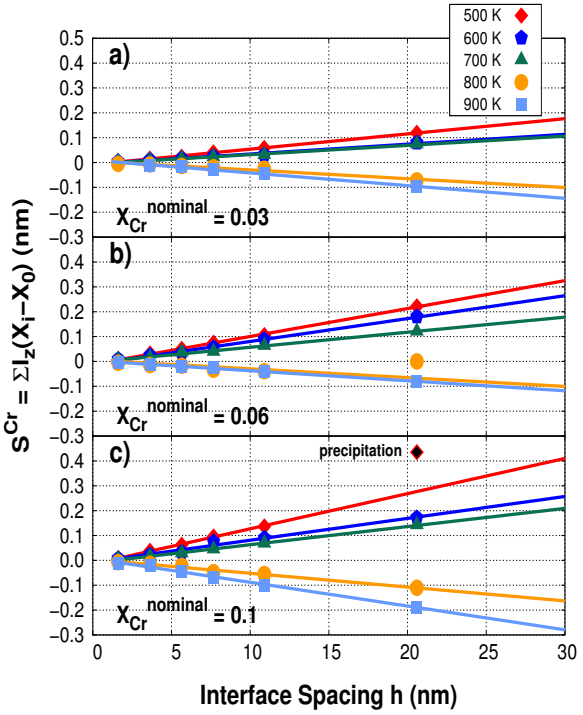
$$S^{Cr} = -\alpha h + \alpha \frac{h}{2} \ln\left(\frac{X_V^{eq}}{a\frac{h^2}{4} + X_V^{eq}}\right) + 2b\alpha \operatorname{arctanh}\left(\frac{h/2}{b}\right)$$

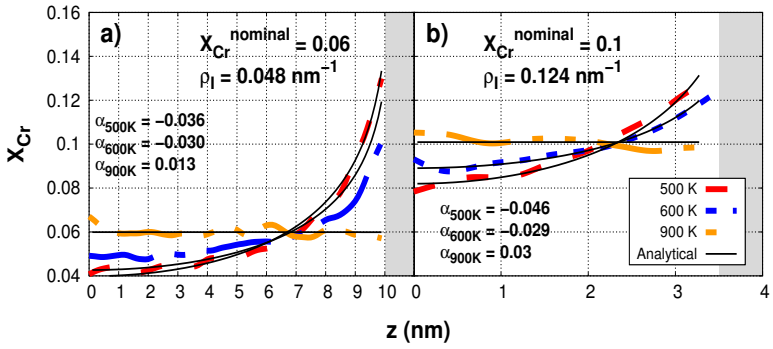
$$b^2 = \frac{h^2}{4} + \frac{X_V^{eq}}{a} \qquad a = \frac{G}{2D_V}$$

In the limit of ideal interfaces:

$$\lim_{X_V^{eq} \to 0} S^{Cr} = \alpha h \left(\ln 2 - 1\right)$$

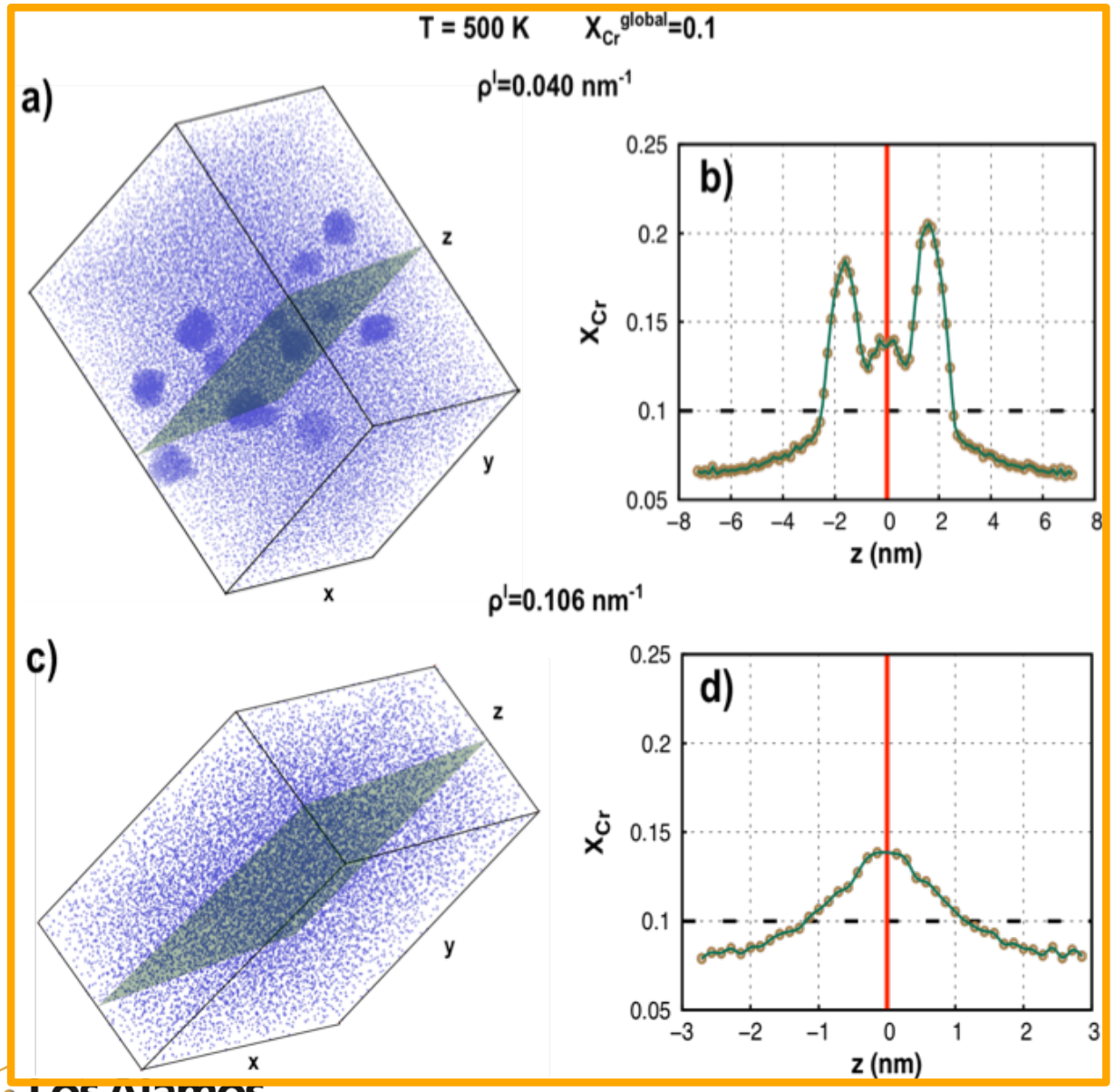



**KMC can help us understand chemical redistribution**

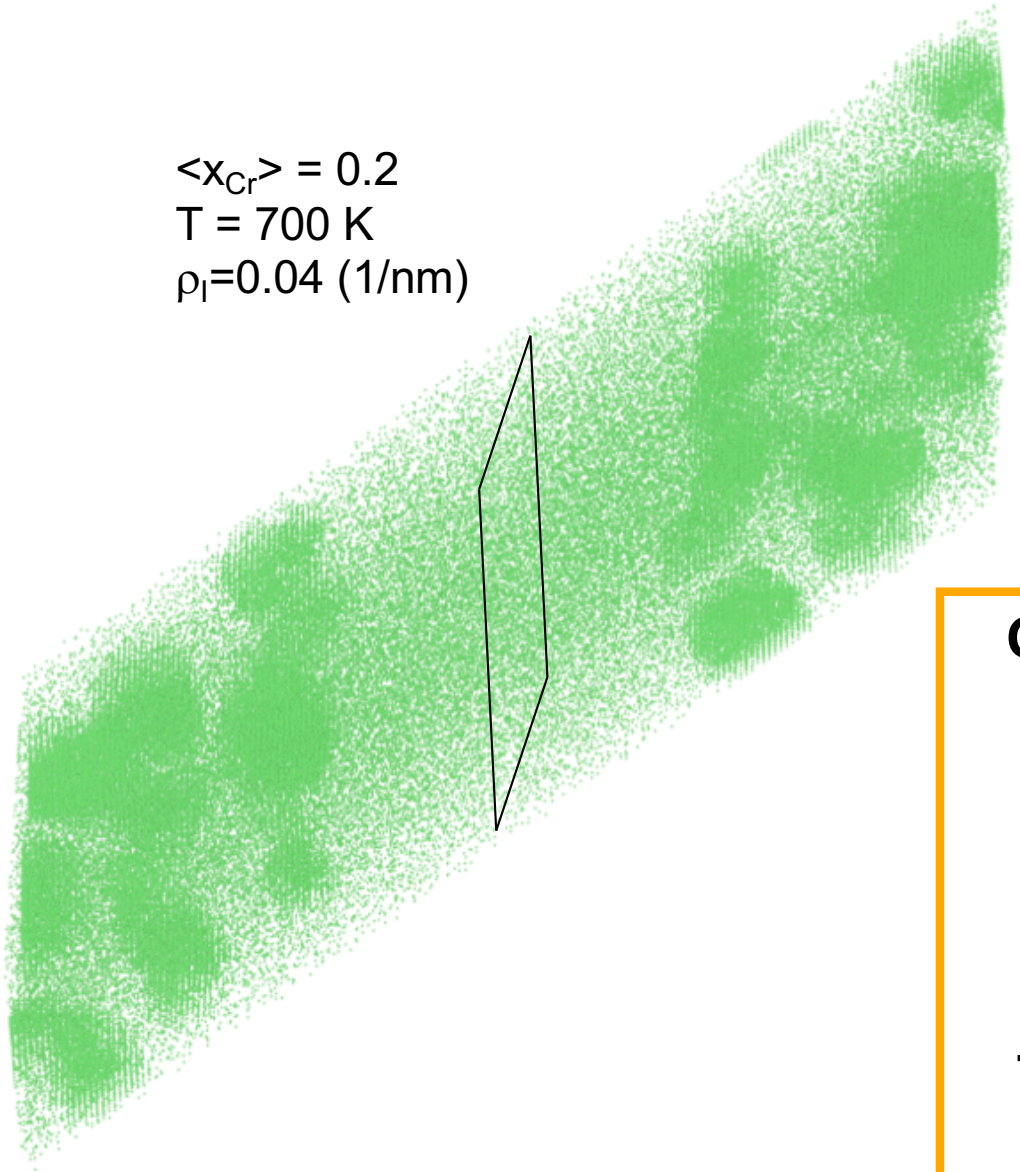
# Radiation-Induced Precipitation




**With the LKMC we can study radiation-induced precipitation, that is harder for the continuous models.**

**Increasing the interface density may inhibit the formation of precipitates**

# Radiation-Induced Precipitation




**Outside the miscibility gap the precipitates form close to the interface if a segregation tendency exists.**

**Inside the miscibility gap precipitates form the farthest from the sink since the defect concentration is the largest.**

# Conclusions

- **Continuum models need free energies and transport coefficients**
- **Atomistic simulations (MD, AMD or KMC) can be used to parametrize the continuum models**
- **Atomistic KMC: an efficient tool to study RIS especially when coupled with *ab initio* calculations**
  - takes into account the real diffusion mechanisms, including the dependence of migration barriers with the local environment and correlation effects → realistic diffusion properties
  - thermal fluctuations → nucleation processes
- **AKMC generates crucial data to incorporate in Phase Field methods**
  - Onsager coefficients
- **AKMC shows that RIS profiles depend strongly on the interface spacing**
- **Drawbacks :**
  - time consuming : limited to relatively short times.
  - Self-Consistent Mean-Field (SCMF) is an alternative approach to calculate phenomenological coefficients that avoids the KMC caveats